# CHEMISTRY OF CIGAR BUTT ODOR. II FURTHER INVESTIGATIONS ON THE DISTILLABLE PORTIONS[1,2]

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In an effort to determine the cause of cigar butt odor, volatile substances were distilled from the butts and particulate matter of smoked cigars. The distillates obtained from both sources were yellow liquids which smelled like cigar butts. Gas chromatographic and spectral studies indicated that the following substances were present in the butt distillate: toluene, 2,4-lutidine, 1,2,3-trimethylbenzene, 1-tridecene, n-amylbenzene, 2-acetylfuran, acetophenone, phenol, p-cresol, ethylbenzene or xylene, indene, 1-acetyl-1-cyclohexane, o-tolunitrile, methanol, acetaldehyde, ethanol, acetonitrile, acetone, methylacetate, allyl alcohol, propionitrile, butanone, isobutyronitrile and butyronitrile. Additional studies have shown the presence of ethylmercaptan, 3,5-lutidine and 2,6-lutidine in the particulate matter distillate. In view of the data thus far obtained, butt odor may be due to a mixture of numerous compounds common to cigar smoke. Since vacuum distillates of butts and particulate matter produce similar chromatograms, it appears that butt odor is caused largely by particulate matter trapped in the butt tobacco.

## INTRODUCTION

Continuing our work on the nature and origin of cigar butt odor, we isolated odorous fractions in distillates from the butts and particulate matter of cigars. Components of some of the fractions were identified by gas chromatographic techniques and infrared and mass spectroscopy. This paper is concerned primarily with the materials occurring in the vacuum distillable fraction of butts and particulate matter. Studies on the amount of water trapped by the butt during smoking were also undertaken.

## EXPERIMENTAL

*Preparation of distillates.* One-thousand cigars supplied by the CMA[5] were smoked in the following manner, (2) one puff every 30 seconds with a puff volume of 35 ml and a puff duration of two seconds. The cigars were smoked to a butt length of 35 mm, which generally required 70 to 90 puffs. The particulate phase was trapped on Cambridge filters held in back of the cigars. The portion of the smoke and the gas phase which passed through the filters was condensed in helical, dry ice-cooled traps and saved for future work. When 48 mm of the cigars was smoked (half the portion to be smoked), fresh Cambridge filters were inserted and the smoking continued to a butt length of 35 mm. The filters were changed because smoking much beyond the halfway point caused saturation of the filter. The butt was removed from the holder and the coal permitted to die by itself as it would in an ashtray under normal smoking conditions. The filters were immediately placed in glass stoppered round bottomed one-liter flasks and the butts were placed in similar flasks after they cooled. The materials were stored in a 10°C refrigerator until they were distilled *in vacuo*.

The flasks of butts and filters were each separately attached to a Dry Ice-cooled cold finger and the distillation was conducted at room temperature for three or four days. Then the temperature was increased over two to three days until steam bath temperature was reached. Distillation was continued at 4 mm Hg for approximately one week. Gradual increase in temperature minimized flashing off of very volatile materials. See **Figure 1** in reference (1) for a diagram of the distillation apparatus. When the cold finger was warmed to melt the frozen material several mls of water with about ¼ ml. of yellow oil floating on the surface were obtained. The oil was pipetted off and the water layer was extracted several times with small amounts of diethyl ether. The oil and the ether extracts were stored in a −10°C freezer until analysis.

In a separate experiment, some low-boiling materials were collected by passing nitrogen gas through the butts and filters and collecting condensed material in a liquid nitrogen-cooled trap. It should be noted that one month of vacuum distillation did not produce odor-free butts. The sharp odor remaining could be removed only by prolonged steam distillation. This steam-distillable fraction is being investigated.

*Gas chromatographic analysis.* Chromatography of the butt and filter distillates on a Perkin-Elmer[6] Model 900 gas chromatograph equipped with ¼ in. x 10 ft. stainless steel column containing 20% SE-30 on silanized chromosorb W produced chromatograms of about 50 peaks (**Figure 1**). The helium flow was 35 ml/min. The column oven was maintained at 100°C for 20 minutes and then programmed at 2°C/min. to 220°C. The injector and flame ionization detector were at 250°C.

Capillary column chromatography was performed on

[1] *For part I of this series see Peck, R. L., S. F. Osman and J. L. Barson* Tobacco Science, *13:38-39 (1969).*
[2] *Portions of this paper were presented at the 24th Tobacco Chemists' Research Conference, Montreal, Canada, October 28-30, 1970.*
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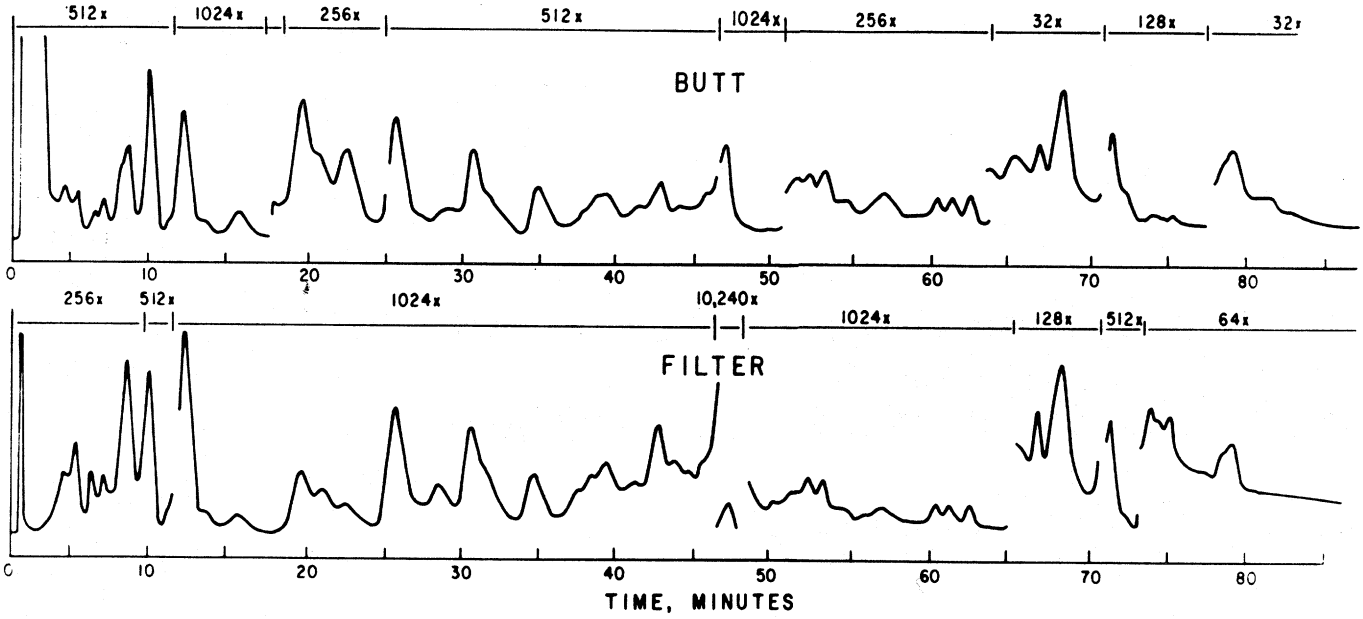


**Figure 1. Comparison of distillates from cigar butts and Cambridge filters (particulate matter). Minor peaks are not shown.**

a Perkin-Elmer Model 900 gas chromatograph fitted with a 150 ft. x 0.02 in. support coated open tubular column coated with OV-225. The oven was programmed at 2°C/min. from 80° to 160°C with an initial isothermal period of 20 minutes. Four-tenths of a micro-liter of neat distillate were injected into the 250°C injector. A flow rate of 4 ml/min. was used. The column was fitted with a 15:1 splitter which led to a 250°C flame ionization detector. Examination of the chromatogram revealed at least 177 peaks, each one corresponding to at least one compound **(Figure 2)**.

Because of the small amount of butt distillate we had

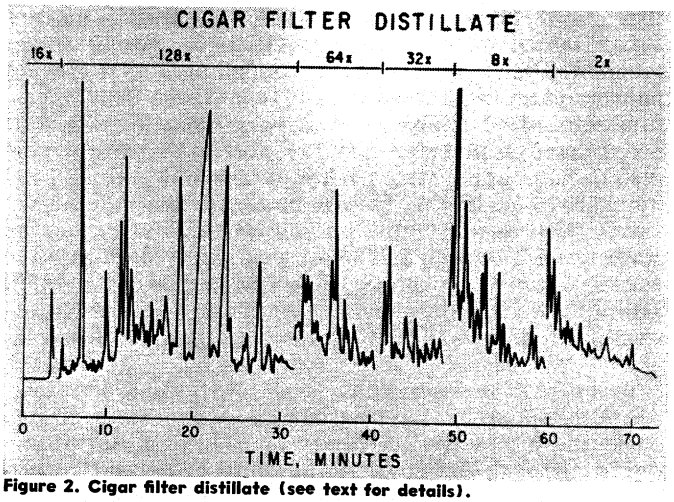


**Figure 2. Cigar filter distillate (see text for details).**

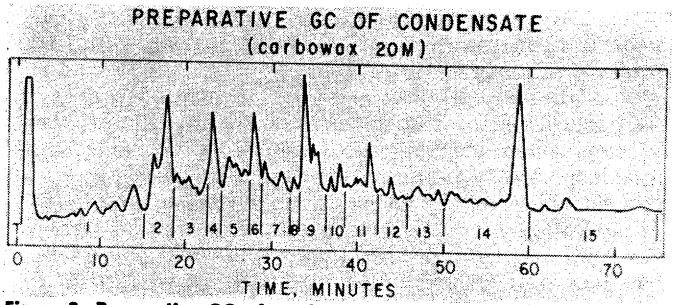


**Figure 3. Preparative GC of condensate on Carbowax 20M (see text for details).**

to work with and the large number of components present, it was sometimes necessary to perform a preliminary separation of the distillate on a preparative gas chromatograph **(Figure 3)**. The material was separated into 15 fractions on an Aerograph Model A-700 Autoprep Gas Chromatograph fitted with a 20 ft. x ¼ in. column containing 20% Carbowax 20M on silanized Chromosorb W. The oven was programmed from 60°C to 190°C over a period of one hour. The fractions were collected in dry ice-cooled receivers while aliquots (0.3 ml.) of the ether solution of the distillate were repetitively injected. To obtain further separation each fraction was subjected to re-chromatography on an Aerograph 1520 analytical gas chromatograph fitted with an SE-30 column under conditions suited for each sample. Effluent peaks were collected in capillary tubes cooled in dry ice. The samples were submitted for analysis on a Consolidated Electrodynamics Corporation Mass Spectrometer Type 21-103C or 21-110. Thin film infrared spectrograms were also made from each sample on a salt plate.

*Determination of water in butts.* Cigars which had been equilibrated with water vapor at 75°F (24°C) in a 60% relative humidity humidor were smoked to a butt length of 35 mm. The weighed butts were ripped open in a flask and the moisture extracted with absolute methanol. Moisture was determined by Karl Fischer titration. This procedure was repeated for 35 mm long butt portions of unsmoked cigars. The unsmoked cigars had a moisture content of 12.5% while smoked butts had a moisture content of 18%, that is, an increase of 50% moisture compared with an unsmoked cigar.

## RESULTS AND DISCUSSION

In addition to the compounds mentioned by Peck, *et al.* (1), we have identified the following compounds occurring in cigar butts in the indicated groups of peaks in Figure 3: group 1, toluene and ethyl benzene or xylene (tentative); group 5, 2,4-lutidine, 1,2,-3-trimethylbenzene, 1-tridecene; group 7, *n*-amyl benzene; group 8, pyrrole; group 9, 2-acetyl-furan, indene (tentative); group 10, 1-acetyl-1-cyclohexene (tenta-

[6] *Mention of specific commercial items does not constitute endorsement by the Department of Agriculture over other items of similar nature not named.*

tive); group 12, acetophenone; group 14, phenol, *p*-cresol, and *o*-tolunitrile (tentative). The following materials were identified in the low-boiling materials entrained in the flow of nitrogen gas; methanol, acetaldyhyde, ethanol, acetonitrile, acetone, pyridine, methyl acetate, allyl alcohol, propionitrile, butanone, isobutryonitrile, butyronitrile.

Ethyl mercaptan was also observed in neat distillates. Its identity was confirmed both by its odor and by cochromatography with authentic material on an OV-225 capillary column and on an SE-30 column. Since the human nose detects ethyl mercaptan at concentrations of one part in 50 billion, it is probably a significant contributor to the odor of cigar butts, although it constitutes less than 0.1% of the cigar butt distillate (determined by relative peak areas).

Examination of **Figure 1** shows a strong similarity between the butt and filter distillates in peak locations and relative peak heights. This similarity suggests that since the butt distillate and the filter distillate smell very much alike that the odor of cigar butts is due in large part to the particulate matter from the smoke which has condensed in the butt.

There has been some question whether the odor of cigar butts is due to the aging of condensed smoke or whether the odor is due to the fresh smoke being slowly carried through to the outside of the butt by the water formed during combustion of the tobacco. The mechanism through which the odor arises will have a bearing on the course taken to remove the odor. If the odor is due to aging of the smoke a method for blocking the chemical reactions of aging would offer a solution. However, if the odor comes about because of fresh combustion products finding their way to the outside of the butt, a method for physically preventing their escape is in order. If a fresh cigar butt, one that does not have an appreciable odor, is torn open, the odor typical of an old cigar butt is very much in evidence. The odor is about as strong as from an old butt. This further supports the conclusion that butt odor is due in a large part to trapped particulate matter.

The compounds listed above represent only the major components of butt and filter distillate. Many other compounds which occur in small concentrations also modify the odor due to their sensitizing and desensitizing effects upon the nose. Pailer, *et al.* (3) identified 53 primary and secondary amines in cigar smoke condensate. Clearly, these materials must occur dissolved in the liquid in cigar butts, but due to their volatility and oxidizability are difficult to detect. On account of their volatility, they probably contribute less to the odor of a butt as it ages. The odor of cigar butts may gain in intensity on aging also due to evaporation of desensitizing agents. In passing, we have recently observed that storing cigar butts in an atmosphere of hydrogen chloride gas effects a marked change in the odor of the butts. The acrid odor of HCl disappeared and the butts had an odor variously described as being "nut like" or like a fresh cigar. We are currently investigating this phenomenon.

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